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# THE FORMATION OF DIMERS VIA THE REARRANGEMENT OF A TERTIARY ALICYCLIC HYDROPEROXIDE

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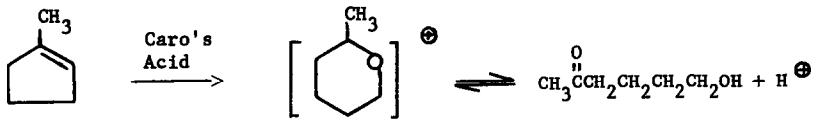
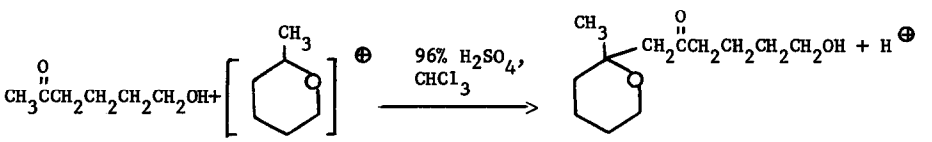
During a recent investigation of tertiary alicyclic hydroperoxide rearrangements in acid we observed that 1-methylcyclopentene, in either Caro's acid ($K_2S_2O_8$ in 96% $H_2SO_4$) or 96% sulfuric acid containing 30% hydrogen peroxide, underwent rearrangement to 6-hydroxy-2-hexanone via the oxonium ion precursor, 2-methyl-5,6-dihydro (4H) pyranyl cation (I).[1]




I

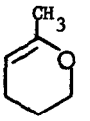
Similar rearrangements have been shown to occur by others.[2-4] Hawkins[5], using 1-methylcyclopentyl hydroperoxide, demonstrated that it underwent rearrangement in dilute sulfuric acid at elevated temperature to yield approximately 15% 6-hydroxy-2-hexanone. Deno and coworkers[6] increased this yield to 90% and studied the rearrangement of a variety of primary, secondary, and tertiary alkyl hydroperoxides in strong acid.

More recent studies in our laboratory have revealed that 1-methylcyclopentyl hydroperoxide (0.0835 mole) in the presence of chloroform (200 cc) and 96% sulfuric acid (3 cc) at 30°C after four hours yielded 1-(2-methyltetrahydropyran-2-yl)-6-hydroxy-2-hexanone, II as one of the major products. This compound presumably resulted from the reaction of the primary product, 6-hydroxy-2-hexanone, with its precursor, I, as illustrated by the following equation.



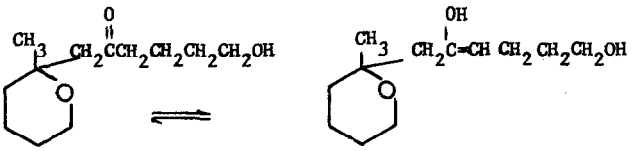

II

The corresponding acetoxy derivative of II was easily formed by treatment with acetic acid. Thermal decomposition of II resulted in the formation of 2-methyl-5,6-dihydro (4H) pyran, III.

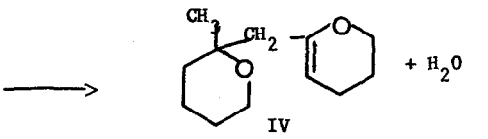


III

Upon standing at room temperature for several hours, compound II underwent cyclization to 2-methyltetrahydropyran-2-yl 5,6-dihydro (4H) pyran-2-yl methane, IV. A possible route to this dimeric product is via enolization of the side chain, followed by cyclization as shown in the equation below:



II



IV

The structure identification of compounds II-IV (and including the acetoxy derivative of II) was based upon a combination of nuclear magnetic and infrared spectroscopy and mass spectrometry all of which are summarized in the following table. Pure fractions of each of these components were isolated by gas chromatographic techniques.

## REFERENCES


1. R. D. Bushick, Tetrahedran Lett., No. 7, 579 (1971.
2. C. U. Pittman, Jr., and S. P. McManus, J. Amer. Chem. Soc., 91, 5917 (1969)
3. W. Pritzkow and K. A. Muller, Chem. Ber., 89, 2321 (1956).
4. F. F. Rust and E. R. Bell, U.S. Pat. 2,717,264 (to Shell Development Co.) Sept. 6, 1955.
5. E. G. E. Hawkins, J. Chem. Soc., 2801 (1950).
6. N. C. Deno, W. E. Billups, K. E. Kramer and R. R. Lastomirsky, J. Org. Chem., 35, 3080 (1970)

TABLE: NMR, Infrared Spectroscopic, and M.S. Results

| Structure | Chemical Shift[2] (ppm) | Infrared[b] (μ) | M.S.[c], (m.e.) |
|---|---|---|---|
| II | 1.20 (s, 3H, $CH_3$) | 2.90 (OH) | $(M^+)-H_2O$ (8%) |
| | 1.56 (m, 10H, $CH_2$) | 5.85 (C=O) | $(M^+)-C_6H_{11}O_2$ (65%) |
| | 2.46 (s, superimposed over m, 4H, $-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-$) | 9.2-9.55 (multiplet adsorption C-O-C, C-O-H) | $(M^+)-C_6H_{12}O_2$ (100%) |
| | 3.57 (m, 4H, $OCH_2$) | | |
| | OH resonance not observed | | |
| II | 1.16 (s, 3H, $CH_3$) | 5.75 ($O-\overset{O}{\overset{\|}{C}}-CH_3$) | $(M^+)$ 256 (7.4%) |
| | | | $(M^+)-C_8H_{13}O_3$ (100%) |
| $-O\overset{O}{\overset{\|}{C}}CH_3$ | 1.55 (m, 10H, $CH_2$) | 5.85 ($C-\overset{O}{\overset{\|}{C}}-C$) | |
| Derivative | 1.97 (s, 3H, $O-\overset{O}{\overset{\|}{C}}-CH_3$) | 8.05 (acetate C-O) | |
| | 2.44 (s, superimposed over m, 4H, $-CH_2-\overset{O}{\overset{\|}{C}}-CH_2$) | 9.2-9.6 (multiplet absorption, C-O-C) | |
| | 3.57 (distorted t, 2H, $OCH_2$) | | |
| | 3.97 (distorted t, 2H, $-\overset{O}{\overset{\|}{C}}-O-CH_2$) | | |
| III | 1.64 (s, with fine splitting, 3H, $CH_3$) | 5.95 (C=C) | $(M^+)$ 98 (100%) |
| | 1.87 (m, 4H, $CH_2$) | 3.25 (C=C-H) | $(M^+)-\overset{O}{\overset{\|}{C}}-CH_3$ (19%) |
| | 3.86 (t, with fine splitting, 2H, $OCH_2$) | 9.4 (=C-O-C) | |
| | 4.30 (distorted t, 1H, C=CH) | | |
| IV | 1.13 (s, 3H, $CH_3$) | 5.98 (C=C) | $(M^+)$ 196 (18.7%) |
| | 1.50-2.00 (m, 10H, $CH_2$) | 3.27 (C=C-H) | $(M^+)-C_6H_9O$ (100%) |
| | 2.14 (s, 2H, $>C-CH_2-\overset{}{\overset{\|}{C}}-$) | 9.2-9.6 (multiplet absorption, C-O) | |
| | 3.56 (distorted t, 2H, $OCH_2$) | | |
| | 3.90 (t, with fine splitting, 2H, $C=C-OCH_2$) | | |
| | 4.45 (distorted t, 1H, C=CH) | | |

a.) Measured in $CCl_4$ with TMS as internal standard
b.) Liquid Film
c.) 9 e.v.